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Effects of tri-solvent and electrospinning condition on the morphology of cellulose acetate nanofibers

Ahmed Saad Montaser[a*], Saad Zaghloul[a], Stephen Kelley[b]

[a]*National Research Centre (NRC), Textile Research and Technology Institute (TRTI), Pre-treatment and Finishing of Cellulose-based Textiles Department (PFCTD), El-Behouth St. (former El-Tahrir str.), Dokki, P.O. 12622, Giza, Egypt*

[b]*Forest biomaterial Department, College of natural resources, North Carolina state university, Raleigh, Campus box 8005, USA.*

Abstract

Producing a valuable nanofibers can occurs by electrospinning, as it consider one of advanced spinning techniques that can obtain functionalized fibers for smart application. The current work demonstrated for new exploration of electrospinning process of cellulose acetate (CA) from trisolvent mixtures. 5% water added to stable CA Electrospinning solution that contains DMAc/AC (1:2). Five different speeds 6, 12, 22, 32 and 40 ml/hr were applied to CA solution. The reflectance of water addition on electrospun fiber properties on fiber diameter and homogeneity was visualized using SEM and Mechanical properties also Contact angles of the preformed nanofibers were characterized. In addition to air permeability test were also evaluated. The obtained fibers showed different morphology against spinning rate. Surface behavior of spun fibers is nearly similar to pristine cellulose acetate (CA) fiber spanned from di-solvent. Spinning rate affects positively on tensile properties and negatively on elongation modulus. The spinning rates indirectly proportional to fiber diameter that reflected on the air permeability. Spinning rate 22ml/hr showed the optimum velocity for spinning from tri-solvent CA solution. Conclusionally, the obtained results open the door for high speed electrospinning process saving time and cost achieving the research target.

Keywords: Electrospinning; Cellulose acetate; Nanofibers; Finishing; Smart fibers.

1. Introduction

The electrospun fiber has gained great importance for various academic and industrial fields applications. Many scientific articles about electrospun polymer fibers have been published in last decade, and many innovative utilizations such as scaffold, filtration, medical wound dressing, drug release, biosensor, and others applications have been reported [1]. Modification of fabrics for enhancing its properties such as antibacterial properties [2-5], Ultraviolet protection [6] wound healing, self-cleaning and military application [7,8], is widely used and many techniques were functionalized for this purpose. Such fibers are recommended due to it have several interesting characteristics, for example a high surface-areato-mass or volume ratio, a small inter-fibrous pore size with high porosity, vast possibilities for surface functionalization, etc. These render electrospun polymeric fibers good candidates for a wide variety of applications [9-11].

Electrospinning process is one of this techniques which may be known as producing nano and micro fibers from solutions through applying high voltage, causes solution ejaculation from positive side (needle) to negative side (collector) [12,13] producing nanofibers and nanowebs utilized for numerous applications such as filtration, biotechnology, textile…..etc. [14]. High voltage not only causes elongation of solution and forming fibers but also affect evaporation of polarized solution as well, forming dry electrospun mate fiber [15]. The ejaculation process controlled with numerous factors as voltage, nozzle-collector distance, viscosity, conductivity, solvent boiling point and speed rate [16]. It is worth to note that Speed rate known as one of electrospinning limitation because homogenous electrospun fibers occasionally combined with low

*Corresponding author e-mail: abohabbiba2012@gmail.com.; (Ahmed Saad Montaser).

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speed rate. Low speed assists solvent to complete evaporation as a result of long duration that helps solvent molecules to evaporate [17]. Cellulose acetate as modified cellulose through acetylation assists researchers to solubilize cellulose in organic solvents, in the same time offers easy spinning process in comparison with pristine cellulose itself [18]. Cellulose acetate (CA) solubilized and electrospun in mono and di-solvents like acetone, chloroform, Dimethyl sulfoxid (DMSO), Dimethylacetamide (DMAc) [19], methanol [18], ethanol….etc. Water mixed with acetone in many reports for producing di-solvent for CA Electrospinning. In this case, water used to increase boiling point of AC to overcome clotting phenomena which resulted from fast boiling point of acetone (b.p of acetone is 39 °C) [20]. It is well known that CA membrane formed from using phase separation, water act as poor solvent for cellulose triacetate which cause membrane precipitation. Precipitation process starts by increasing viscosity by solvent replacement, followed by shrinking process as a result from chain entanglement [21].

From this point of view, water as phase separation solvent for cellulose triacetate used to produce a new solution with new properties at Electrospinning process. Herein, a small portion of water 5% added to stable cellulose triacetate bi-solvent (DMAc/AC). The viscosity and conductivity of the new solution examined against parent solution. Complete study used to visualize the effect of water on the spin-ability process of CA 2.54. The produced electrospun fibers that obtained using different speed rate were examined under SEM for visualizing fiber morphology and homogeneity in addition to fiber diameter. Mechanical properties were evaluated using tensile strength, elongation modulus as well. The relationship between fiber diameter and spinning rate and permeability was also evaluated.

2. Experimental

2.1. Materials

Cellulose acetate 2.54 was kindly provided by Eastman Company, USA, sodium hydroxide, sodium carbonate, acetic anhydride, Sulphoric acid, sodium citrate, and ethyl alcohol, other solvents and double distilled water were of laboratory grade chemicals. N,N′-dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO) and Dimethylacetamide (DMAc) and acetone were purchased from Sigma-Aldrich.

2.2. Methods: Electrospinning of Cellulose acetate

Cellulose acetate 2.54 solubilized in Ac/DMAc (2:1) for 3 hr, a small portion of water 5% added to the prepared solution followed by vigorous stirring for more 2 hr. Syringe glass 10 ml filled with prepared CA solutions and connected with the positive part of Electrospinning, the negative part connected to rotated collector as appear in below. Syringe pump worked at different speed rates 6, 12, 22 and 32 ml/hr. the prepared electrospun fibers collected and cute for the following characterizations [22].

2.3. Characterization of produced CA electrospun fibers

Electrospun CA fibers homogeneity and fiber diameter examined through scanning electron microscope (SEM). Microscopic investigations on CA fabric samples were carried out using a Philips XL30 scanning electron microscope (SEM). Images were taken at different magnifications (from 1509 to 3,0009), using secondary electrons (SE) in accordance with the clarity of the images [23]. Samples were fixed with carbon glue and metalized by gold vapor deposition to record images. The conductivities, viscosity and surface tension of spinning solutions were measured with a digital conductivity meter (DDS-307A) and NDJ-79 Digital brookfield viscometer . To achieve that, the conductive electrode was soaked into the solution completely at room temperature, and then the stabilized readings were recorded. The mechanical properties were measured with a Electrospun CA tensile strength Elongation and young module testing using instrone machine under speed rate 10 mm/min with the samples size of 25mm × 40mm [24]. The water contact angles (WCA) of the samples were analyzed by a (phoenix series version 0.5) contact angle tester equipped with a high-resolution TV camera [25]. Air permeability was tested using Gurley method [26].

3. Results and discussion

The electrospun fibers can be prepared to form numerous structures by utilizing solvent with high vapor pressure or deliberately adding salt to the polymer solution and leach the latter out once the fibers are dried. The produced structure of electrospun fibers has a high surface to volume ratio that makes electrospun fibers ideal for filtration, odor absorption and various smart textile applications [27-30].

Optimum condition for spinning CA fibers from di-solvent AC/DMAc solution (2:1) was speed rate 6ml/hr, nozzle-holder distance 10 cm and applied voltage 15kV. To visualize the effect of tri-solvent on speed rate and fiber morphology, five more solution from tri-solvent was prepared and examined. The CA solutions parameter from viscosity conductivity and surface tension were examined and displayed at table 1. Adding water to CA solution increased

conductivity and surface tension. This may attributed to increment in polarity of CA solution. While viscosity increased due to phase separation to CA solution

Optical images of CA electrospun fibers illustrated in Fig. 1.a. Electrospinning of cellulose acetate from binary solvent (DMAc/ AC) showed a wide and homogeneous spun sheets. The homogeneity was attributed to completely soluble solution and equal distribution resulted from equal effect of electrical field on the spun solution from needle to collector. The tri-solvent (DMAc/Ac/ 5% H2O) showed a thick centered bundle sheet. As shown in fig .1.b, c, d and e. the thick fiber resulted from phase separation.

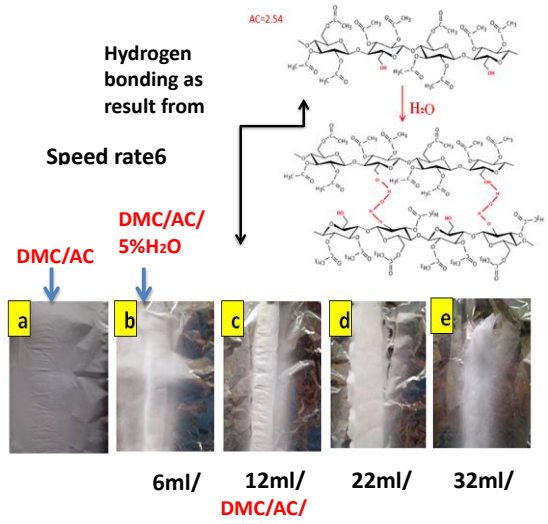

Figure 1: Optical images for produced Electrospun fibers using binary and trinary solvent at different speed rate.

3.1. Scanning Electron Microscoope (SEM).

Surface morphology of electrospun fibers after treatment process was often monitored by the making use of SEM as shown below in fig. 2. Spinning CA from tri-solvent showed impressive results at different spinning rates compared to di-solvent that frequently used in literatures. The tri-solvent showed an efficient spinning process even at a high speed rate which reached 32 ml/min. SEM results showed morphology and fiber homogeneity at ascending spinning rated ranged from 6-32 ml/hr at a constant concentration 10% CA 2.54. It's clearly appears that spinning at low speed showed single homogenous cylindrical fibers of CA, with 1.3 µ diameter. The fiber diameter increased by increasing spinning rate until reaching 3.6 µm. After that, Electrospinning process formed droplet and no spinning fiber can be obtained. The speed rate reversely fit fiber diameter. It's attributed to the short time need consumed to reach the collector, by increasing the time which affects negatively on solvent evaporation causes increasing in fiber diameter. Increasing speed rate in presence of tri-solvent and water molecules assist exhibiting a stable electrospun fiber even at high speed rate as indicated before. The phase separation process may act as helping factor assist separation of CA chains from the solvent that helping fast solvent evaporation. On the same time, hydrogen bonding exhibited as a result of water molecules assist chain entanglement that permit spinning process even at high spinning rates.

For fiber homogeneity, at early speed rates 6 and 12 ml/hr, thin fiber obtained and the size increasing with increasing spinning rate until reaching 12 ml/hr. beaded fibers with heterogeneous fibers obtained at 22 ml/hr, it express the formation of coagulations as a result of high speed. Molten fibers appear at high spinning rate a result of poor solvent evaporation. After this rate dispersed droplet appears and no chance for fiber formation.

3.2. Contact Angles

For further functionalization of nano-fiber to obtain hydrophobic surface for water repellant, Contact angle of cellulose acetate was measured using single water droplet. Contact angle consider the main measurement used to estimate the water repellant properties of fabrics [31,32].

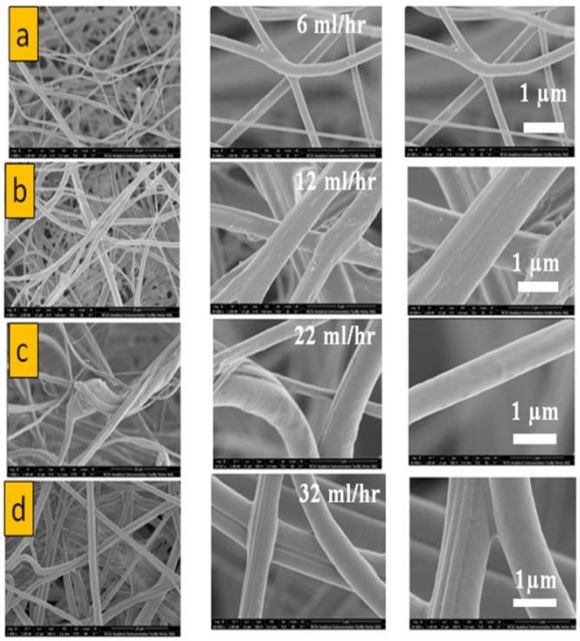

Figure 2: Scanning Electron Microscope of Cellulose acetate with different speeds.Where :a) 6 ml/hr, b) 12 ml/hr , c) 22 ml/hr
and d) 32 ml/hr.

Contact angle of CA spun at low spinning rate appropriate with contact angle in the literature. It's showed at Fig.3. High contact angle at early seconds as a result of acetate groups which as hydrophilic groups that showed high surface tension forming high contact angle. The high spinning rates showed the same

behavior with lower contact angle in comparison with the low spinning rates. It confirms that the surface physical properties of CA still like the pristine one with low spinning rates. The decrement in the angle may be due to inhomogeneity surface structure of the high spun rate in comparison with the low speed. The surface homogeneity affects positively on contact angle as shown in the literatures.

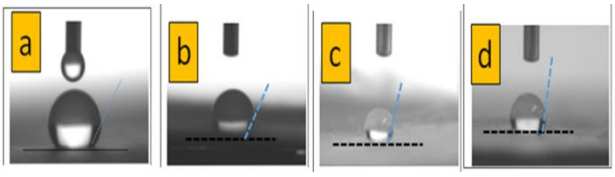

Figure 3: Contact angles of Cellulose acetate with different speeds; Where: a) 6 ml/hr, b) 12 ml/hr, c) 22 ml/hr and d) 32 ml/hr.

3.4. Mechanical properties

Mechanical properties have been utilized for investigation the effect of treatment on the produced fibers. There are three parameters which represented as the main components of mechanical properties viz., maximum strength, elongation at break % and young modulus as shown in figure 4. Mechanical properties of CA electrospun fibers with different speed rated appear in Fig. 4. Tensile strength showed ascending data with increasing spinning rate. As mentioned by increasing spinning process it's showed centered spinning on the collector. This centering affects positively on chain reinforcement which reflects on ascending results of tensile strength until reaching 22 ml/hr then decreased. The decrement results from molten fibers confirm poor spun fiber results at this speed rate. Otherwise, the elongation results showed a decrement in data with increasing spinning rate. The phase separation and chain entanglement resulted from hydrogen bonding increase side-by-side force interaction rather than head to tail chain enforcement, which appears clearly on tensile and appears negatively on elongation percent's. Besides, phase separation may disturb CA chains order that affects negatively on elongation properties.

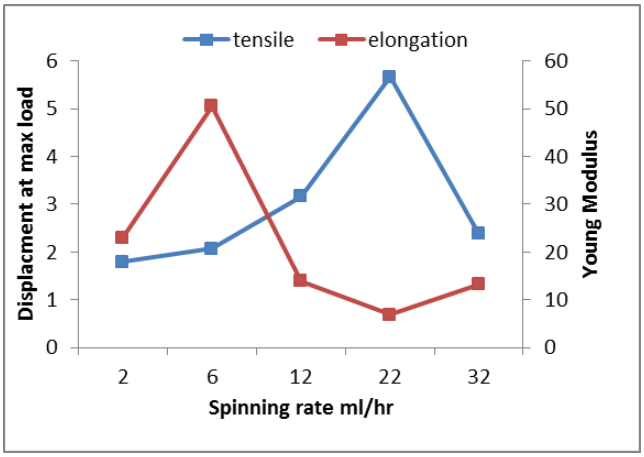

Figure 4: Mechanical Properties of Electro spun cellulose acetate fibers.

3.5. Air Permeability

Air permeability test (Fig.5) showed increasing permeability with increasing spinning rate. It shows low permeability at low spinning rates and high permeability at high ones. This attributed to the small fiber diameter of the CA fibers at low spinning rate and thick fibers at high rates. It's confirmed that porosity and fiber –fiber spaces increasing with fiber diameter with reflects positively on air permeability results. The various results of permeability candidates the high spinning rates to different applications depends on permeability requirement.

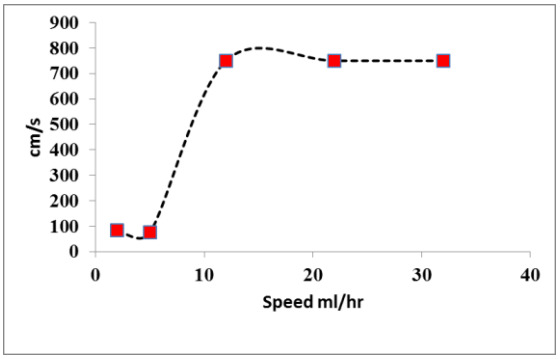

Figure 5: Air permeability of the prepared cellulose acetate Nano fibers

4. Conclusion

Nano fibers produced by electrospinning technique at specific conditions using tri-solvent, New physical phenomena come up as a result of using tri-solvent in spinning process of Cellulose acetate (CA) solution. Low water percent added to cellulose triacetate solution provides impressive electrospun fibers at high spinning rates (22ml/hr) as a result of phase separation and chain entanglement. Scanning electron microscope analysis indicates that the obtained fibers showed different morphology against spinning rate. Surface behavior of spun fibers is nearly similar. Spinning rate affects positively on tensile properties and negatively on elongation modulus. The spinning rates indirectly proportional to fiber diameter that reflected on the air permeability results, the work goal is successfully achieved as shown in previous results.

5. Conflict of interest

The authors declare that there is no conflict of interes

6. Acknowledgment

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